

PATENT SPECIFICATION

NO DRAWINGS

861,371



Date of Application and filing Complete Specification: April 10, 1959.

No. 12165/59.

Application made in United States of America on April 25, 1958.

Complete Specification Published: Feb. 22, 1961.

Index at Acceptance:—Class 2(3), 14.

International Classification:—C07f.

COMPLETE SPECIFICATION

Process for the Preparation of Cyclopentadienyl Manganese Tricarbonyl Compounds.

We, ETHYL CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 100 Park Avenue, New York 17, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of cyclopentadienyl manganese compounds and more particularly to the manufacture of cyclopentadienyl manganese tricarbonyl compounds.

Cyclopentadienyl manganese tricarbonyl compounds have been found to be exceptionally effective antiknock agents for use in fuel for spark plug ignition internal combustion engines. These compounds not only have exceptional effectiveness as antiknock agents but also many of these compounds have auxiliary properties which make them practical and desirable for commercial use. These auxiliary properties include high solubility in fuels, such as gasoline, and thermo-stability either alone or in gasolines which makes these compounds entirely satisfactory for use under the widely varying conditions to which gasoline and other fuels are normally subjected. Possibly of even greater importance, these compounds, unlike iron compounds, do not tend to form any appreciable deposits on the engine pistons, valves and spark plug surfaces and likewise are not abrasive to the engine parts as are characteristic of iron compounds.

According to the invention we provide an improved process for the manufacture of cyclopentadienyl manganese tricarbonyl compounds comprising reacting a manganous compound with a cyclopentadiene-hydrocarbon and carbon monoxide in the presence of a transition metal carbonyl and an ele-

ment selected from Group II or III-A of the Periodic Table according to Deming, herein referred to as the Periodic Table.

It has now been found that cyclopentadienyl manganese tricarbonyl compounds can be produced in excellent yields by reacting a manganous compound simultaneously with a cyclopentadiene hydrocarbon and gaseous carbon monoxide at a pressure of from 25 to 8000 psig if the reaction is conducted in the presence of a transition metal carbonyl, i.e. of a metal of Group V-B, VI-B, VII-B or VIII of the Periodic Table, and also in the presence of an element of Group II or III-A of the Periodic Table.

More specifically, our process comprises reacting the cyclopentadiene hydrocarbon and manganous compound with carbon monoxide, preferably in a liquid medium which is a solvent for the manganese compound, in the presence of from about 0.01 to 50 moles percent of the transition metal carbonyl. Somewhat lower concentrations can be employed but the benefits of the metal carbonyl are also diminished. Likewise, higher concentrations of the metal carbonyl can be employed but the resulting improvement in the process is not greatly increased and is accordingly uneconomical. The process is preferably conducted at a temperature of from 75° to 250°C., although the process can be conducted over a temperature range of 0° to 300° or such temperatures wherein the reactants and products are stable. The manganous compound and cyclopentadiene hydrocarbon are preferably employed in about stoichiometric quantities, it being frequently preferred to employ the cyclopentadiene in excess, e.g. from 50 to 30 percent. The carbon monoxide can be used at from subatmospheric to superatmospheric pressures although it is preferred to use pressures ranging from 25

[Price 3s. 6d.]

psig to 8000 psig. Higher pressures can be employed to increase the reaction rate, although, very surprisingly, the very high pressures, i.e. above about 10,000 psig, appear to lower the product yield.

The cyclopentadiene hydrocarbon can be used in monomer form or can also be used as a dimer. When using the dimeric cyclopentadiene hydrocarbon it is frequently desirable to conduct the reaction at the more elevated temperatures, i.e. at temperatures above about 150°C.

The effectiveness of the transition metal carbonyl compounds in the process of this invention is very surprising and in fact the reaction mechanism is not understood. In the absence of the transition metal carbonyl, the yield of the cyclopentadienyl manganese tricarbonyl compounds is very low, usually below about 5 percent based upon the manganese compound. In contrast, in the presence of even small quantities of the transition metal carbonyl, the yields of the desired cyclopentadienyl manganese tricarbonyl increase many fold. This unexpected phenomenon is apparently not due to the mere donation of carbonyl groups to the manganese metal by the transition metal carbonyl employed in the process since the reaction does not proceed readily in the absence of gaseous carbon monoxide. The presence of very high pressures of carbon monoxide results in an apparent depressing effect on the reaction would indicate that the reaction mechanism has something to do with the metal carbonyl decomposition and therefore it is possible that some decomposition is necessary to the actual effectiveness of the metal carbonyl in this reaction.

The compounds which can be made by the process of this invention are any cyclopentadienyl manganese tricarbonyl compounds, including substituted cyclopentadienyl compounds, such as the indenyl and fluorenyl derivatives. Typical examples of such compounds are cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, *n*-butylcyclopentadienyl manganese tricarbonyl, isobutylcyclopentadienyl manganese tricarbonyl, *n*-decylcyclopentadienyl manganese tricarbonyl, phenylcyclopentadienyl manganese tricarbonyl, methylphenylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl and fluorenyl manganese tricarbonyl. For fuel use, the preferred compounds are those containing up to 12 carbon atoms in the cyclopentadienyl group.

The element of Group II or III-A of the Periodic Table is employed in a concentration of from about molar equivalence to about 100 percent excess, based upon the manganese compound. Even greater excesses can be employed without affecting

the reaction but, in general, this is uneconomical and creates problems in recovery of the product. Lesser quantities, i.e. 0.5 mole per mole of manganese compound, can be used but poorer results are obtained.

The liquid medium suitable for the process of this invention can be any solvent or complexing agent for the manganese compound. In general, suitable solvents are ethers, amines, amides and nitriles. The ethers can be either aliphatic or aromatic, such as dimethyl ether, diethyl ether, methyl-ethyl ether, anisole, diphenyl ether and, any ether which is liquid at the reaction temperature and pressure employed. Preferred ethers are the cyclic ethers and the ethylene glycol ethers. Typical examples are dioxane, tetrahydrofuran, ethylene glycol dimethyl ether, and corresponding higher alkyl ethers, such as diethyl, methyl ethyl and dibutyl ethers. Typical examples of diethylene glycol dialkyl ethers are the dimethyl, diethyl, methyl ethyl, dibutyl and the triethylene glycol ethers including the dimethyl, diethyl and diisopropyl ethers. The preferred ethylene glycol dialkyl ethers have alkyl groups containing from 1 to 6 carbon atoms.

Suitable amines for use as solvents in this invention are propyl amine, diethyl amine, di-*n*-propyl amine, dibutyl amine, triethyl amine, triisopropyl amine, and other amines having from 2 to 10 carbon atoms per alkyl group. Aromatic amines are also suitable, such as aniline, methyl aniline, dimethyl aniline, and similar compounds. A particularly suitable amine solvent is dicyclohexylamine.

Typical examples of suitable amides are formamide, and the mono- and dialkyl formamides containing alkyl groups having from 1 to 6 carbon atoms, such as *N,N*-dimethyl formamide. Other suitable amides are cyclic amides, such as *N*-methyl pyrrolidone and other alkyl pyrrolidones, and amides of inorganic acids, such as hexamethyl phosphoramide.

Suitable nitriles which can be employed as solvents in this invention are acetonitrile, propionitrile and butyronitrile.

The liquid medium can be employed in a wide range of concentration from about 0.5 mole, based upon the manganese compound, to about 30 moles. Higher dilution of the reaction mixture can be employed except that no appreciable improvement in the reaction is obtained and considerably greater difficulty is encountered in the recovery of the desired product.

Any of the manganese compounds can be employed, for example the oxide, sulphide, halides, sulphate, carbonate or nitrate. Of these, the halides are preferred and especially the chloride. The organic compounds of manganese are also useful in this invention, for example manganous

phide and carbon monoxide (1800 psig) in the presence of 1.5 mole equivalent of aluminium (powdered) and 20 mole percent of nickel carbonyl. The reaction is conducted in tetrahydrofuran solvent (10 moles per mole of manganous sulphide) at a temperature of 90°C. The fluorenyl manganese tricarbonyl is recovered by distillation.

10 In the above examples the cyclopentadiene hydrocarbon and metal carbonyl have been reacted directly with the manganous compound. With certain of the metal carbonyls which form complexes with cyclopentadiene, 15 such as the complex dicyclopentadienyl di-iron tetracarbonyl, the complex can be used directly in the reaction.

WHAT WE CLAIM IS:—

1. Process for the manufacture of cyclopentadienyl manganese tricarbonyl compounds comprising reacting a manganous compound with a cyclopentadiene hydrocarbon and carbon monoxide in the presence of a transition metal carbonyl and an element selected from Group II or Group III-A of the Periodic Table as hereinbefore defined.

2. Process according to claim 1, wherein the reaction is carried out at a pressure from 25 to 8000 pounds per square inch gauge. 30

3. Process according to claims 1 or 2, wherein the cyclopentadiene hydrocarbon and manganous compound are reacted with carbon monoxide, preferably in a liquid medium which is a solvent for the manganous compound, in the presence of from about 0.01 to 50 moles percent of the transition metal carbonyl. 35

4. Process according to claims 1, 2, or 3, wherein the reaction is effected at a temperature between 0° and 300°C., preferably 75° to 250°C. 40

5. Process for the manufacture of cyclopentadienyl manganese tricarbonyl compounds, substantially as herein described. 45

6. Cyclopentadienyl manganese tricarbonyl compounds when prepared by the process according to any one of the preceding claims.

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formate, acetate, propionate, butyrate, oxalate, tartrate, and other salts of organic acids having up to 10 carbon atoms.

5 The elements of Groups II and III-A of the Periodic Table preferably employed in the process in an active form. Best results are obtained when the metal is finely divided, that is having a particle size ranging from
10 about 5 microns up to particles having 2 to 4 millimetres in thickness. The metal preferably should have a clean surface, essentially uncontaminated with an oxide coating. It is found that powdered metals available commercially are very suitable.
15 The following examples further illustrate our process. All parts are given as parts by weight.

EXAMPLE I

20 To a reaction vessel equipped with means for agitating the reaction mixture was added 4 parts of manganous chloride, 2 parts of magnesium metal powder, 4 parts of methylcyclopentadiene dimer, 1 part of iron pentacarbonyl, and 50 parts of N,N-dimethyl
25 formamide. The reactor was then sealed and pressurized to 3500 psig with gaseous carbon monoxide and the reaction mass heated with agitation to a temperature of 195°C. for one hour. The reactor was
30 then cooled and the reaction product steam distilled to recover the desired methylcyclopentadienyl manganese tricarbonyl. The product was obtained in about 28 percent yield, based upon the manganous chloride
35 charged to the reactor. This compares with only about 2 percent yield when the reaction is conducted in the absence of iron pentacarbonyl. The purified methylcyclopentadienyl manganese tricarbonyl has exceptional
40 antiknock effect when used in gasoline fuels.

EXAMPLE II

Example I was repeated except that the reaction temperature was maintained at 225°C. and 3 hours of reaction time was
45 employed. Similar results were obtained.

EXAMPLE III

Example I was repeated except that 2 parts of iron pentacarbonyl were employed and essentially the same yield of the desired
50 product was obtained.

EXAMPLE IV

Example I was repeated except that 8 parts of methylcyclopentadiene dimer was charged to the reaction and essentially
55 equivalent results were obtained.

EXAMPLE V

Example I was repeated except that a lower pressure of carbon monoxide was employed, i.e. 1000 psig. Similar results
60 were obtained except that the yield of methylcyclopentadienyl manganese tricarbonyl was somewhat lower than in Example I.

EXAMPLE VI

65 High pressures of carbon monoxide were

employed to illustrate its effect on the formation of the desired product. When employing a pressure of 8200 psig of carbon monoxide, the yield dropped drastically, given only 0.5 percent yield based upon
70 the manganous compound charged. With pressures of 12,900 psig of carbon monoxide the yield was only 0.2 percent.

EXAMPLE VII

Example I is repeated except the cyclopentadiene monomer is reacted with manganous acetate and carbon monoxide (1500 psig) in the presence of metallic beryllium (2 moles) and vanadium carbonyl (1 mole percent). The reaction is conducted in
80 N-methyl pyrrolidone at 150°C.

EXAMPLE VIII

N-butyl cyclopentadiene is reacted with manganous oxide and carbon monoxide (2000 psig) in the presence of calcium metal and chromium hexacarbonyl according to the procedure of Example I. Diethylene glycol dimethyl ether (5 moles per mole of the manganous compound) is employed as the solvent and the reaction is conducted at
90 250°C. The *n*-butylcyclopentadienyl manganese tricarbonyl is recovered in good yield.

EXAMPLE IX

Example I is repeated except that *n*-decylcyclopentadiene is reacted with manganous sulphate and carbon monoxide (1000 psig) in the presence of 3 mole equivalents of zinc and 15 mole percent of manganese pentacarbonyl based upon the manganous sulphate. The manganous sulphate is
100 employed in 30 percent excess relative to the *n*-decylcyclopentadiene. The reaction is conducted in acetonitrile solvent (a saturated solution of manganous sulphate) at a temperature of 115°C.
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EXAMPLE X

Methylphenylcyclopentadiene is reacted with manganous iodide and carbon monoxide (5000 psig) in the presence of 2 mole equivalents of cadmium metal and 10 mole
110 percent of $\text{Fe}_2(\text{CO})_9$. This reaction is conducted in the dicyclohexylamine solvent at a temperature of 140°C. The methylphenylcyclopentadienyl manganese tricarbonyl is distilled from the reaction product,
115 after removal of the solvent. The final distillation of product is conducted in the presence of an equal volume of a high-boiling hydrocarbon (a petroleum fraction) to suspend the inorganic impurities.
120

EXAMPLE XI

Indene is reacted with manganous oxalate in hexamethyl phosphoramide in the presence of 5 mole equivalents of boron and 1 mole percent of cobalt carbonyl. The
125 reaction is conducted at 300°C. The indenyl manganese tricarbonyl product is recovered in excellent yield.

EXAMPLE XII

Fluorene is reacted with manganous sul- 130